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(54) **Polymer composition for pipes**

(57) HDPE compositions comprising a bimodal polymer and a nucleating agent, for production of pipes

having increased pressure resistance, and the use of such compositions in the production of pipes.

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Description

[0001] This invention related to polymers for the production of pipes having increased pressure resistance.

[0002] Polyethylene pipe materials are often classified according to the design stress rating (ISO/DIS 12162.2). This is the circumferential stress the pipe is designed to withstand for at least 50 years without failure. The design stress rating is determined at different temperatures in terms of Minimum Required Strength (MRS) according to ISO/TR 9080. Thus, MRS8.0 means that the pipe can withstand an internal pressure of 8.0 MPa at 20°C for 50 years. Similarly, MRS10.0 means that the pipe can withstand a pressure of 10.0 MPa at the conditions above.

[0003] Pipes fulfilling the MRS8.0 requirements are typically made of either unimodal or bimodal ethylene polymers. The pipes fulfilling the MRS 10.0 requirements are typically made of bimodal ethylene polymers. The corresponding polyethylene materials are often referred to as PE80 and PE100 materials, respectively.

[0004] Bimodal ethylene polymers have different densities and molecular weights depending on the intended use of the polymer. Thus, a bimodal ethylene polymer often used in pressure pipes comprises a bimodal ethylene polymer and a carbon black additive, having a density of about 955-961 kg/m³ and an MFR₅ of about 0.3-0.9 g/10 min. Another bimodal ethylene polymer used in pipe manufacture has a density of about 937-943 kg/m³ and an MFR₅ of about 0.5-1.0 g/10 min.

[0005] Bimodal PE100 materials have excellent properties compared to unimodal materials due to a high concentration of the tie chains which connect crystal lamellae. However, in natural bimodal materials the crystallites formed are large and the boundary layers between crystallites, consisting of segregated amorphous material, are relatively wide. Under these circumstances fewer tie chains will connect different crystallites.

[0006] It has been known to use nucleating agents to increase the crystallinity and decrease the crystal size of polypropylene. Polyethylene, however, has been known to have a much higher crystallization rate than polypropylene and nucleating agents have not been effective in it.

[0007] "PE100 Resins for Pipe Applications: Continuing the Development into the 21st Century" (Scheirs et al, TRIP Vol 4, No. 12, 1996) provides a summary of different PE100 grades on the market. It stresses the importance of the molecular structure, in specific molecular weight distribution and comonomer distribution, of the material.

[0008] EP-A-739937 discloses a pipe made of bimodal ethylene polymer, having a specific stress cracking resistance and impact strength. The material also has a specific stiffness and MFR.

[0009] The present invention is based on the surprising finding that a small amount of a nucleating agent in bimodal ethylene polymer composition significantly increases the pressure resistance of a pipe made from the polymer composition. While an increase of the pressure resistance has been observed with unimodal ethylene polymers also, the effect on bimodal compositions is dramatically and unexpectedly stronger. Typically, the nucleating agent also produces a reduction in the flexural modulus of the polymer.

[0010] According to the present invention a polymer composition for producing pipes with increased pressure resistance, comprises a bimodal polymer formed of:

- i) a low molecular weight ethylene polymer or copolymer and
- ii) a high molecular weight ethylene polymer or copolymer

and a nucleating agent, the alpha-olefin of the ethylene alpha-olefin copolymer preferably being selected from propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and cyclic olefins, and constituting between 0.5 and 10 weight % of the copolymer. A carbon-black additive may also be present in the composition. The low molecular weight component (i) suitably comprises 30-70% by weight of the bimodal polymer.

[0011] In addition to the constituents mentioned above, the composition may also contain minor amounts of other components, such as prepolymer, carrier resins of masterbatches or similar, as disclosed in, e.g. WO-A-96/18677. The amount of such components should not exceed 5% of weight of the composition.

[0012] The bimodal polymer may be produced by blending the low and high molecular weight components in an extruder, or in a single- or multi-step polymerization process.

[0013] The nucleating agent may be a pigment or an additive which acts as a nucleus for a polyethylene crystal. Examples of such nucleating agents are the α - and β -phthalocyanine blue pigments and the phthalocyanine green pigment.

[0014] The bimodal ethylene polymer typically has a density of 930-965 kg/m³ and a melt index MFR₅ measured at 190°C under 5 kg load of 0.1-1.2 g/10 min, preferably of 0.15-1.0 g/10 min. It comprises preferably 40-55% and more preferably 43-48% by weight of low molecular weight component (i) and preferably 60-45% and more preferably 57-52% by weight of high molecular weight component (ii). It also preferably has a number average molecular weight M_n between about 8000 and 15000 g/mol, a weight average molecular weight M_w between about 180000 and 330000 g/mol, a polydispersity index M_w/M_n between about 20 and 40, and a content of units derived from the alpha-olefin comonomer between about 0.4 and 3.5% by mole.

[0015] The low molecular weight polymer (i) preferably has a weight average molecular weight of about 5000-50000 g/mol and a melt index MFR₂ measured under 2.16 kg load between about 50 and 2000 g/10 min. Preferably it is a homopolymer of ethylene, containing less than 2%, preferably less than 1%, more preferably less than 0.5% and most preferably less than 0.2% by mole units derived from higher alpha-olefin comonomers. Thus, the density of the low molecular weight ethylene polymer (i) should be 960-980 kg/m³, preferably 965-980 kg/m³ and more preferably between 970-980 kg/m³.

[0016] The high molecular weight polymer (ii) typically has a weight average molecular weight of about 300000-1000000 g/mol. Moreover, it is preferably a copolymer of ethylene and a higher alpha-olefin, the content of the alpha-olefin comonomer units being about 0.7-7.0% by mole. In particular, the molecular weight of the high molecular weight polymer (ii) should be such that when the low molecular weight ethylene polymer (i) has the melt index and density specified above, the bimodal polymer has the melt index and density as specified above.

[0017] The polymers (i) and (ii) may be produced using any known method where ethylene is polymerized in the presence of a Ziegler or a single site catalyst. Thus, they may be produced by a solution polymerization process, a slurry polymerization process or a gas phase polymerization process. The bimodal polymer may, moreover, be produced in a multistage process, such as that disclosed in EP-B-517868 or WO-A-96/18662. Typically, the polymerization takes place in the presence of a Ziegler catalyst, such as disclosed in EP-A-688794 and EP-A-949274. It is also possible to use a single site catalyst, such as that disclosed in FI-A-960437.

[0018] Preferably, the low molecular weight ethylene polymer (i) is produced in one stage of a multistage polymerization process and the high molecular weight ethylene polymer in another stage of the process. In particular, the low molecular weight ethylene polymer may be produced in a continuously operating loop reactor where ethylene is polymerized in the presence of a polymerization catalyst and a chain transfer agent, such as hydrogen. An inert aliphatic hydrocarbon, like isobutane or propane is used as a diluent. Preferably no, or only traces of a, higher alpha-olefin comonomer is present.

[0019] The hydrogen concentration should be selected so that the low molecular weight ethylene polymer (i) has the desired MFR. Typically, the molar ratio of hydrogen to ethylene is then between 0.1 and 1.0 mol/mol, preferably between 0.2 and 0.8 mol/mol. It is advantageous to operate the loop reactor using propane diluent in so called supercritical conditions, where the operating temperature exceeds the critical temperature of the reaction mixture and the operating pressure exceeds the critical pressure of the reaction mixture. A suitable range of temperature is then from 90 to 110°C and a suitable range of pressure is from 50 to 80 bar.

[0020] The slurry is intermittently or continuously removed from the loop reactor to a separation unit, where the hydrocarbons and especially the chain transfer agent are separated from the polymer. The polymer containing the active catalyst is introduced into a gas phase reactor, where the polymerization proceeds in the presence of additional ethylene, alpha-olefin comonomer and optionally, chain transfer agent to produce the high molecular weight ethylene polymer (ii). The polymer is intermittently or continuously withdrawn from the gas phase reactor and the remaining hydrocarbons are separated from the polymer. The polymer collected from the gas phase reactor is the ethylene polymer (1).

[0021] The conditions in the gas phase reactor are selected so that the bimodal polymer has the desired properties. Typically, the temperature in the reactor is between 70 and 100°C and the pressure is between 10 and 40 bar. The hydrogen to ethylene molar ratio ranges from 0.001 to 0.1 mol/mol and the alpha-olefin comonomer to ethylene molar ratio ranges from 0.05 to 0.5 mol/mol.

[0022] The nucleating agent may be any compound or mixture of compounds capable of nucleating the crystallization, such as a pigment having a nucleating effect or an additive used only for nucleating purposes. Examples of the first category of compounds are phthalocyanine blue or green pigments (e.g. PB15:1, PB15:3, PG7), isoindolinone and isoindoline pigments (e.g. PY109, PY110, PO61), benzimidazolone pigments (e.g. PO62, PO72), quinacridone pigments (e.g. PY19), benzimidazolone pigments (e.g. PY180, PY181), quinophtalone pigments (e.g. PY138), chinacridone pigments (e.g. Pigment Violet PV19) and azoheterocyclus pigments (e.g. PO64). Examples of the second category of compounds are dibenzylidene sorbitol derivatives and dibenzylidene xylitol derivatives.

[0023] The nucleating agent may also be a polymeric additive, such as a polymer of vinylcyclohexane or 3-methyl-1-butene. In such case, the polymeric additive, which preferably has a melting point above 200°C, may be blended into the bimodal polymer by conventional means in an extruder, or it may be prepolymerized on the catalyst as disclosed e.g. in WO 99/24478.

[0024] A characteristic feature of the invention is that a low amount of nucleating agent is needed to achieve the desired effect, usually significantly less than used previously in the art. This results in savings in raw material costs. Moreover, because a smaller amount of the additive is needed, there are less likely to be problems related to plate-out of the additive. The exact amount of the nucleating agent depends on which compound is used as the nucleating agent. The composition usually contains from about 1 to about 1500 ppm, preferably from 10 to 1000 ppm by weight of the nucleating agent.

[0025] Compositions according to the invention may also contain other additives known in the art, for instance sta-

bilizers such as hindered phenols, phosphates, phosphites and phosphonites, pigments such as carbon black, ultramarine blue and titanium dioxide, additives such as clay, talc, calcium carbonate, calcium stearate, and zinc stearate, UV absorbers, antistatic additives like those sold under trade name Lankrostat, and UV-stabilizers which may be hindered amines such as that sold under trade name Tinuvin 622.

5 [0026] According to one preferred embodiment of the invention, the bimodal polymer has a density of 943-953 kg/m³ and a melt index MFR₅ of 0.2-0.6 g/10 min. It comprises 45-55%, preferably 47-52% of low molecular weight homopolymer component (i) having MFR₂ of 300-700 g/10 min and 55-45%, preferably 53-48% by weight of high molecular weight component (ii). Additionally, the it may contain 0-5% of other ethylene polymers having MFR₂ of 0.2-50 g/10 min and density of 920-980 kg/m³. The composition comprises 40-800 ppm of phtalocyanine blue as the nucleating agent. Further, the composition may contain 0-1000 ppm titanium dioxide, 0-5000 ppm ultramarine blue, 100-2000 ppm antioxidant (like Irganox 1010), 0-2000 ppm process stabilizer (like Irgafos 168), 0-3000 ppm calcium stearate or zinc stearate and 0-5000 ppm UV-stabilizer (like Tinuvin 622).

10 [0027] According to another preferred embodiment of the invention, the bimodal polymer has a density of 937-941 kg/m³ and a melt index MFR₅ of 0.7-1.1 g/10 min. It comprises 41-47%, preferably 42-46% of low molecular weight homopolymer component (i) having MFR₂ of 200- 500 g/10 min and 53-59 %, preferably 54-58 % by weight of high molecular weight component (ii). Additionally, it may contain 0-5% of other ethylene polymers having MFR₂ of 0.2-50 g/10 min and density of 920-980 kg/m³. The composition comprises 40-800 ppm of phtalocyanine blue as the nucleating agent. Further, the composition may contain 0-1000 ppm titanium dioxide, 0-5000 ppm ultramarine blue, 100-2000 ppm antioxidant (like Irganox 1010), 0-2000 ppm process stabilizer (like Irgafos 168), 0-3000 ppm calcium stearate or zinc stearate and 0-5000 ppm UV-stabilizer (like Tinuvin 622).

20 [0028] The classification of a composition comprising the bimodal polymer and additives and pigments, but not comprising the nucleating agent, can, by adding the nucleating agent into the composition as prescribed by the invention, be increased from a value of MRS 10.0 to a value of MRS 11.2, which connotes a major improvement in pressure resistance of pipe made from the composition.

25 [0029] The invention is illustrated by the following Examples, in which MFR is measured according to ISO 1133 at 190°C. The load has been indicated as a subscript, i.e. MFR₂ denotes that the measurement has been carried out under a load of 2.16 kg.

[0030] The pressure test values originate from slow crack propagation resistance test, performed according to ISO 1167. The resulting figure indicates how many hours the pipe can withstand a certain pressure at a certain temperature without a failure. The temperature and pressure are indicated as test parameters, e.g. 20°C/12.4 MPa indicates that the test was performed at 20°C temperature with 12.4 MPa pressure within the pipe. Briefly, the test procedure is as follows.

30 [0031] Pipes with 32 mm diameter and a thickness of 3 mm, internally filled with water, are mounted in a water bath and connected to a device which allows the internal water pressure to be adjusted and controlled within a range of +2 to - 1%. The temperature of the water bath can be selected and is kept constant to within a mean of +/- 1°C. The time to pipe failure is registered automatically.

Example 1

40 [0032] The base polymer is a natural bimodal material produced in two cascaded CSTR slurry reactors using a polymerization catalyst containing Mg and Ti as active ingredients. In the first reactor diluent, ethylene and hydrogen were added together with the catalyst and triethylaluminum cocatalyst, so that an ethylene homopolymer with MFR₂ of 500 g/10 min was produced. The slurry was withdrawn from the first reactor, excess hydrogen and ethylene were removed and the polymerization was continued in the second reactor by adding ethylene, hydrogen and 1-butene comonomer. The slurry was withdrawn from the reactor, the hydrocarbons were removed and the polymer was compounded in an extruder and pelletized. The MFR₅ of the final polymer was 0.4 g/10 min and the density 948.

45 [0033] In runs 1-5 the polymerization catalyst was non silica-based and the production split (between first and second reactors) was 52/48. In runs 6-9 the polymerization catalyst was silica-based and the production split was 48/52.

50 [0034] Various pigment formulations were then worked into the pelleted material on a Buss Kneader 100-11D, and the thoroughly mixed compositions were extruded into 32 mm diameter pipes of 3 mm wall thickness which were subjected to the above described ISO 1167 test. Of the various components of these formulations, the titania, the ultramarine and the yellow pigment "PY93" are devoid of nucleating effect. The results are shown in Table 1 below.

TABLE 1

Run	Temp/Stress	Pigment Formulation (ppm) (total composition basis)	Hours to Failure
1	80°/5.7 MPa	None	370
2	80°/5.7 MPa	PY93*: 1500 ppm TiO ₂ : 600 ppm	91
3	80°/5.7 MPa	PB15.1**: 800 Ultramarine: 2500 TiO ₂ : 900	1280
4	80°/5.7 MPa	PB15.3**: 1775 TiO ₂ : 945	1510
5	80°/5.7 MPa	PB29***: 3800 TiO ₂ : 370 PY93: 50	130
6	20°/12.4 MPa	None	83†

7	80°/5.7 MPa	None	460††
8	20°/12.4 MPa	PB15.1: 375 PB29: 1275 TiO ₂ : 405	7873†
9	80°/5.7 MPa	PB15.1: 375 PB29: 1275 TiO ₂ : 405	>17800 (running)

* o-benzotoluidide, 3,3''-[(2-chloro-5-methyl-p-phenylene) bis (immocarbonylacetonilideneazo)] bis [3',4-dichloro-(8Cl)], a yellow pigment.

** denote $\alpha(.1)$ - and $\beta(.3)$ - Cu phthalocyanine blue.

*** ultramarine

† mean of two tests.

†† mean of five tests.

Example 2

[0035] The base polymer is a natural bimodal material produced in a process comprising a cascade of a loop reactor and a gas phase reactor, in presence of a silica based catalyst. In the loop reactor diluent, ethylene and hydrogen were added together with the catalyst and triethylaluminum cocatalyst, so that an ethylene homopolymer with MFR₂ of 350 g/10 min was produced. The slurry was withdrawn from the first reactor, hydrocarbons were removed and the polymerization was continued in the gas phase reactor by adding ethylene, hydrogen and 1-butene comonomer. The polymer was withdrawn from the reactor, the hydrocarbons were removed and the polymer was compounded in an extruder and pelletized. The MFR₅ of the final polymer was 0.93 g/10 min and the density 940. The production split was 44% in the loop reactor, 56% in the gas phase reactor.

[0036] Test batches were prepared and subjected to test as in Example 1. The results are shown in Table 2 below.

TABLE 2

Temp/Stress	Pigment Formulation (ppm) (Total Composition Basis)	Hours to Failure
20°/10.0 MPa	None (3000 ppm Tinuvin 622 added as UV stabilizer)	208
80°/4.6 MPa	None (3000 ppm Tinuvin 622 added as UV stabilizer)	0.9
20°/10.0 MPa	PB29:1200 PB15.1: 660 PG7*:230 TiO ₂ :4400 (plus 2000 ppm Tinuvin 622 as UV stabilizer)	Test concluded at 3000
80°/4.6 MPa	PB29:1200 PB15.1:660 PG7:230 TiO ₂ :4400 (plus 2000 ppm Tinuvin 622 as UV stabilizer)	3032

* phthalocyanine green

Example 3 (comparative)

[0037] The base polymer is a natural unimodal material produced in a gas phase process in presence of a silica based chromium catalyst. Ethylene, 1-butene and polymerization catalyst were introduced into the reactor operated in such conditions that a polymer resin having a MFR₅ of 0.9 g/10 min and the density 939 kg/m³ was obtained.

[0038] Test batches were prepared and subjected to test as in the previous Examples.
The results are shown in Table 3 below.

TABLE 3

Temp/Stress	Pigment Formulation (ppm) (Total Composition Basis)	Hours to Failure
20°/11.0 MPa	PY93 : 990	230
20°/11.0 MPa	PB29:1200 PB15.1:660 PG7:230 TiO ₂ : 4400	400

[0039] It will be observed that when the base PE resin is unimodal the effect of the phthalocyanine blue nucleating agent is not significantly greater than that of the non-nucleating yellow pigment, and is significantly lower than its effect at comparable conditions when (Table 2) the base PE resin is bimodal.

Claims

1. A polymer composition comprising an ethylene homopolymer or an ethylene alpha-olefin copolymer for producing pipes with increased pressure resistance, wherein the polymer is a bimodal polymer comprising
 - i) a low molecular weight ethylene polymer or copolymer and
 - ii) a high molecular weight ethylene polymer or copolymer
 and a nucleating agent.
2. A polymer composition according to claim 1, **characterized in that** the alpha-olefin of the ethylene alpha-olefin copolymer is selected from the group of propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and cyclic olefins.
3. A polymer composition according to claims 1 or claim 2, **characterized in that** the alpha-olefin comonomer content is between 0.5 and 10 weight %.
4. A polymer composition according to any of claims 1 to 3, **characterized in that** a carbon-black additive is present.
5. A polymer composition according to any preceding claim, **characterized in that** the density is between 930 and 965 kg/m³.
6. A polymer composition according to any preceding claim, **characterized in that** the melt index MFR5 measured at 190°C under 5 kg load is between 0.1 and 1.2 g/10 min.
7. A polymer composition according to any preceding claim, **characterized in that** the polymer composition comprises 30-70% of said low molecular weight ethylene polymer or copolymer and 70-30% of said high molecular weight ethylene polymer or copolymer.
8. A polymer composition according to any preceding claim, **characterized in that** the number average molecular

weight Mn is between 8000 and 150000 g/mol.

9. A polymer composition according to any preceding claim, **characterized in that** the weight average molecular weight Mw is between 180000 and 330000 g/mol.
10. A polymer composition according to any preceding claim, **characterized in that** the polydispersity index Mw/Mn is between 20 and 40.
11. A polymer composition according to any preceding claim, **characterized in that** the low molecular weight ethylene polymer or copolymer has a weight average molecular weight of between 5000 and 50000 g/mol.
12. A polymer composition according to any preceding claim, **characterized in that** the low molecular weight ethylene polymer or copolymer has a melt index MFR2 measured under 2.16 kg load of between 50 and 2000 g/10min.
13. A polymer composition according to any preceding claim, **characterized in that** the low molecular weight ethylene copolymer has a comonomer content of less than 2 mol %.
14. A polymer composition according to any preceding claim, **characterized in that** the low molecular weight ethylene polymer or copolymer has a density between 960 and 980 kg/m³.
15. A polymer composition according to any preceding claim, **characterized in that** the high molecular weight ethylene polymer or copolymer has a weight average molecular weight of between 300000 and 1000000 g/mol.
16. A polymer composition according to any preceding claim, **characterized in that** the high molecular weight ethylene copolymer has a comonomer content of 0.7 to 7.0 mol %.
17. A polymer composition according to any preceding claim, **characterized in that** the nucleating agent is a pigment.
18. A polymer composition according to any preceding claim, **characterized in that** the nucleating agent is a phthalocyanine blue or green pigment.
19. A polymer composition according to any of claims 1 to 16, **characterized in that** the nucleating agent is a dibenzylidene sorbitol derivative.
20. A polymer composition according to any of claims 1 to 16, **characterized in that** the nucleating agent is a dibenzylidene xylitol derivative.
21. A polymer composition according to any of claims 1 to 16, **characterized in that** the nucleating agent is a polymeric additive.
22. A polymer composition according to any preceding claim, **characterized in that** the nucleating agent is present in an amount of between 1 and 1500 ppm.
23. A polymer composition comprising an ethylene homopolymer or an ethylene alpha-olefin copolymer for producing pipes with increased pressure resistance, wherein the polymer is a bimodal polymer comprising
 - i) a low molecular weight ethylene polymer or copolymer and
 - ii) a high molecular weight ethylene polymer or copolymerand a nucleating agent, whereby the pressure resistance MRS according to ISO/TR 9080 is at least 10% higher than for the same polymer composition not comprising a nucleating agent.
24. Use of a polymer composition comprising an ethylene homopolymer or an ethylene alpha-olefin copolymer, whereby the polymer is a bimodal polymer and comprises
 - i) a low molecular weight ethylene polymer or copolymer and
 - ii) a high molecular weight ethylene polymer or copolymer and a nucleating agent for producing pipes with increased pressure resistance.



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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 8173

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08L
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